Measurement of Titanium Dioxide Nanoparticles in Sunscreen using Single Particle ICP-MS

Introduction
Titanium dioxide (TiO₂) nanoparticles are commonly used in sunscreens as part of the formulation to block the sun's harmful UV rays. As the use of nanoparticles in consumer products has increased, concern has risen as to the health and environmental effects of nanoparticles. Since sunscreens contact skin and wash off in water, the TiO₂ nanoparticles can find their way into biological and environmental systems. As a result, there is a need to measure both the size and size distribution of these nanoparticles in sunscreens so as to assess their impact on human health and the environment.
Traditionally, nanoparticle size characteristics have been determined by several methods, including field flow fractionation (FFF), dynamic light scattering, and microscopy, among others. Recently, single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) has been gaining attention as a way to both measure and characterize nanoparticles. Advantages of SP-ICP-MS include speed and the amount of information which can be gained from the analysis.

This work will focus on characterizing TiO₂ nanoparticles in sunscreens using SP-ICP-MS with a simple sample preparation.

**Experimental**

**Sample Preparation**

Sunscreen products were purchased at a local store and had the label information shown in Table 1. For each sample, 15 mL of sunscreen was added to a 50 mL container and mixed for three minutes to create a homogeneous sample. Next, 0.2 g of each homogenized sample was transferred to another container, followed by addition of 200 mL 1% Triton-X solution. These solutions were sonicated until all aggregates appeared to be broken up (5-10 minutes). After sonication, serial dilutions were performed on the samples with deionized water to produce particle concentrations of 100,000 – 200,000 particles/mL (as measured during analysis).

Transport efficiency determination was performed with gold nanoparticles (50, 80, 100 nm, nanoComposix, San Diego, California, U.S.A.) which were prepared by dilution in deionized water to a final nominal concentration of 100,000 particles/mL. All standards were sonicated for five minutes prior to analysis to ensure that any agglomerated particles were dispersed. Forty nanometer TiO₂ (US Research Nanomaterials Houston, Texas, U.S.A.) spikes were added to various samples to verify the accuracy of the TiO₂ size measurements.

Calibration standards for titanium consisted of 2, 5, and 10 ppb standards prepared in deionized water from a 1000 mg/L titanium standard (PerkinElmer, Shelton, Connecticut, U.S.A.).

**Results and Discussion**

To characterize the Ti background of the system and reagents, a blank solution consisting of only the reagents (i.e. Triton X-100 in deionized water) was analyzed, with the resulting signal shown in Figure 1. While a few signal spikes are seen, the majority of the Ti background is below two counts, which demonstrates the cleanliness of the system.
To determine the ability to see TiO$_2$ particles in a sunscreen matrix, the sunscreen without any TiO$_2$ particles was analyzed. Figure 2A shows the TiO$_2$ particle signal from a sunscreen which does not contain TiO$_2$ (according to its label). Aside from a few spikes, the background is equivalent to the blank (Figure 1).

Next, this sunscreen solution was spiked with 40 nm TiO$_2$ particles at a concentration of 6.65 µg/L; the resulting signal is shown in Figure 2B. Since each spike represents a particle, it is evident that TiO$_2$ particles can easily be seen in a sunscreen matrix.

Furthermore, the most frequent size particle was 40 nm, demonstrating the accuracy of the measurement.

Figure 3 shows the TiO$_2$ particle size distribution for a 20,000 times-diluted sunscreen (Sunscreen 5).

With the ability to accurately measure TiO$_2$ particles in sunscreen established, other sunscreen samples were analyzed three times; the results are shown in Table 4.

Figure 2. TiO$_2$ signals from a sunscreen which does not contain TiO$_2$ (2A), and spiked with 40 nm TiO$_2$ (2B) particles. The screen shot shows the processed data of spiking 40 nm TiO$_2$ into a sunscreen which does not contain any TiO$_2$ nanoparticles (2C).

Figure 3. Processed data for 20,000 times-diluted sunscreen which contains TiO$_2$ nanoparticles.
### Conclusion

This work has demonstrated the ability to measure TiO$_2$ nanoparticles in commercial sunscreen samples. Using both the NexION 350 ICP-MS and the Syngistix Nano Application Software Module, the analysis is simple and rapid, yet can clearly differentiate the TiO$_2$ content among different samples.

### Consumables Used

<table>
<thead>
<tr>
<th>Component</th>
<th>Description</th>
<th>Part Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium Standard</td>
<td>1000 ppm, 125 mL</td>
<td>N9303806</td>
</tr>
<tr>
<td>Sample Uptake Tubing</td>
<td>0.38 mm id (green/orange), flared, 2-stop</td>
<td>N0777042</td>
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<tr>
<td>Drain Tubing</td>
<td>1.30 mm id (gray/gray), Santoprene, 2-stop</td>
<td>N0777444</td>
</tr>
</tbody>
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*This sunscreen contains no nanoparticles, as shown in Table 1.

These results indicate that the sunscreens had TiO$_2$ nanoparticles ranging from 24 – 67 nm, with similar size distributions in each. However, Sunscreen 5 is clearly different from the others: the smaller dilution factor required to obtain less than 200,000 particles/mL indicates that fewer TiO$_2$ particles are present in this sample than the others.